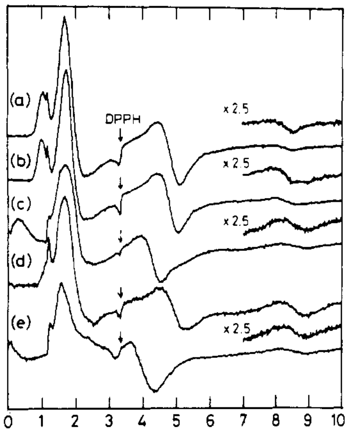

Figure 2. ESR spectra of Cr^{III}TPP complexes at 77 K: (a) Cr^{III}(TPP)Cl in CHCl$_3$, (10 mM; total volume 0.2 mL); (b) mixture used for curve a plus TGE (1 M; total volume 0.2 mL); (c) mixture used for curve b plus Me$_4$NOH (1 M; 60 μL); (d) mixture used for curve a plus Me$_4$NOH (1 M; 60 μL); (e) mixture used for curve a plus methanol (60 μL).

The results presented here provide not only a synthetic method of a new type of chromium(III) porphyrin complex but also an insight into the axial coordination mode of Cr(III)-substituted cytochrome P450 if it is prepared.

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Redox Asymmetry and Metal–Metal Coupling in Pyrazine-Bridged Ruthenium Dimers

Sir:

Elucidation of the nature and extent of electronic coupling in mixed-valence dimers continues to present a challenging theoretical and experimental problem.[1-3] The pyrazine-bridged diruthenium decaammine species [Ru(NH$_3$)$_5$]$_2$pyz^{5+} (the Creutz–Taube ion[4]) presents a particularly intriguing case since it does not appear to fall squarely into either the predominantly valence-localized Robin and Day class II category or the fully delocalized class III category.[5,6]

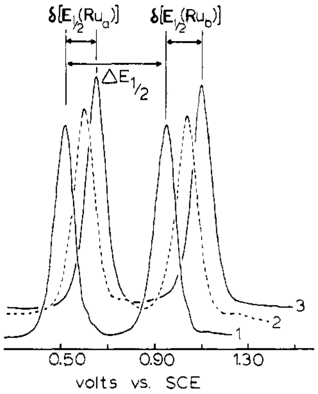

Figure 1. Differential pulse polarograms and identification of experimental quantities: (1) Creutz–Taube ion, [(NH$_3$)$_5$Ru]$_2$pyz$^{4+/5+/6+}$; (2) *trans*-pyRu$_b$(NH$_3$)$_4$(pyz)Ru$_a$(NH$_3$)$_5$$^{4+/5+/6+}$; (3) *trans*-2,6-Me$_2$pyzRu$_b$(NH$_3$)$_4$(pyz)Ru$_a$(NH$_3$)$_5$$^{4+/5+/6+}$. Measurements made in 0.1 M (TEA)PF$_6$ in acetonitrile at 2 mV/s with a 10–mV pulse amplitude and 0.2-s drop time.

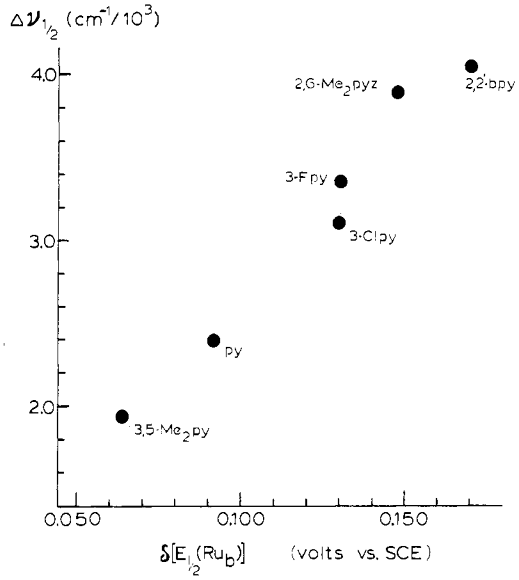

Figure 2. $\Delta\nu_{1/2}$, bandwidth at half-maximum for intervalence-transfer band vs. $\delta[E_{1/2}(\mathrm{Ru_b})]$, shift in second redox wave relative to Creutz–Taube ion second wave: 3,5-Me$_2$py = 3,5-dimethylpyridine; py = pyridine; 3-Cl-py = 3-chloropyridine; 2,6-Me$_2$pyz = 2,6-dimethylpyrazine; 2,2'-bpy = 2,2'-bipyridine.

We wish to report here on a novel approach to the investigation of metal–metal coupling in mixed-valence dimers and its preliminary application to a series of pyrazine-bridged species related to the Creutz–Taube ion. Experimentally the approach involves the systematic introduction of redox asymmetry into a dimer using a *trans*-LRu(NH$_3$)$_4$ fragment on one end of the molecule, where L is varied over different nitrogen heterocycles so as to "tune" the redox potential of that end. Variations of the redox potential at the *other* end are then observed, and their magnitude is taken as being indicative of the extent of coupling between the sites. This technique has been applied previously to the case of metal–ligand interactions in complexes where a discrete ligand-localized reduction wave is observable such as *trans*-LRu^{II}(NH$_3$)$_4$(pyd)$^{3+}$, where pyd = *N*-methyl-4,4'-bipyridinium or *N*-methyl-4-cyanopyridinium, and in complexes such as M(bpy)$_2$L$_2$$^{2+}$, where M = Ru, Os and bpy = 2,2'-bipyridine.[7,8]

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Table I. Electrochemical and Spectroscopic Data for the Complexes Studied Thus Far

L	$E(\mathrm{Ru_b})$,[a] V	$E(\mathrm{Ru_a})$,[a] V	$\Delta E_{1/2}$,[a] V	m[b]	ρ[c]	$10^{-3}E_{\mathrm{IT}}$,[d] cm^{-1}	$10^{-3}\Delta\nu_{1/2}$(obsd), cm^{-1}	$10^{-3}\Delta\nu_{1/2}$(calcd),[e] cm^{-1}
trans-$\mathrm{LRu_b(NH_3)_4pyzRu_a(NH_3)_5}$								
NH_3	0.848	0.418	0.430			6.25	1.44	3.8
3,5-Me_2py	0.912	0.493	0.419	1.17	1.08	6.15	1.94	3.8
py	0.940	0.505	0.435	0.95	0.97	6.25	2.39	3.8
3-Cl-py	0.978	0.522	0.456	0.80	0.89	6.71	3.18	3.9
3-F-py	0.979	0.525	0.454	0.82	0.91	6.63	3.35	3.9
2,6-Me_2pyz	0.996	0.543	0.453	0.84	0.92	7.43	3.88	4.1
bpy	1.019	0.565	0.454	0.86	0.93	8.67	4.04	4.4
$\mathrm{(bpy)_2Ru_bCl(pyz)Ru_a(NH_3)_4L}$								
NH_3	0.965	0.545	0.420			9.8	4.9	4.1
py	1.012	0.735	0.277	0.25[f]	0.50	8.2	4.9	4.0
3-Cl-py	1.005	0.770	0.235	0.18[f]	0.42	7.5	5.1	3.9

[a] Potentials determined via differential pulse polarography vs. SCE in acetonitrile; typical reproducibility ±3 mV. [b] $m = \delta[E_{1/2}(\mathrm{Ru_a})]/\delta[E_{1/2}(\mathrm{Ru_b})]$ relative to the 4+/5+/6+ Creutz–Taube ion. [c] Calculated from eq 6. [d] Intervalence-transfer band maximum as determined by Br_2 oxidation of the fully reduced dimer in acetonitrile. [e] Calculated from the theoretical equation $\Delta\nu_{1/2} = [2310(E_{\mathrm{IT}} - \Delta E)]^{1/2}$ (see ref 2, 9, 19), where energies are in cm^{-1} and ΔE is approximated as $\Delta E_{1/2}$(dimer) − $\Delta E_{1/2}$(Creutz–Taube ion) in the first series and by simple comparison of monomer potentials for the second series. [f] $m' = \delta[E_{1/2}(\mathrm{Ru_b})]/\delta[E_{1/2}(\mathrm{Ru_a})]$ relative to $\mathrm{(bpy)_2RuCl(pyz)Ru(NH_3)_5}^{3+/4+/5+}$.

Figure 1 illustrates the way in which the electrochemical data are analyzed, and Table I gives a summary of the results for the complexes studied thus far.

There are several interesting points revealed by the data. First, it is seen that the bandwidth at half-maximum, $\Delta\nu_{1/2}$, of the intervalence transfer band for the first series increases gradually from 1.44×10^3 to 4.04×10^3 cm^{-1} as a stronger and stronger perturbation $\delta[E_{1/2}(\mathrm{Ru_b})]$ is applied. At the high-$\delta[E_{1/2}(\mathrm{Ru_b})]$ end of the series, $\Delta\nu_{1/2}$ is found to be reasonably in line with the theoretical prediction made by Hush theory. This indicates that a class II electronic structure has been attained. Figure 2 illustrates the gradual widening of the band as $\delta[E_{1/2}(\mathrm{Ru_b})]$ is increased. A similar, though more scattered, correlation is also obtained between the bandwidth and $\Delta E_{1/2}$. The trend in Figure 2 is expected to be due to the combined effects of the redox asymmetry and the decreased electron density for π back-bonding to the pyrazine bridge arising from competitive π back-bonding to L in the *trans*-$\mathrm{LRu_b^{II}(NH_3)_4pyz}$ fragment. That this latter effect is operative but not predominant is demonstrated by the spectral results for the symmetrically substituted *trans*-$\mathrm{[pyRu(NH_3)_4]_2pyz^{5+}}$ dimer. In this case we find $E_{\mathrm{IT}} = 5.87 \times 10^3$ cm^{-1} and $\Delta\nu_{1/2} = 1.82 \times 10^3$ cm$^{-1}/10^3$. Comparison with the data in Table I shows that the band has indeed widened about halfway to the value obtained for the asymmetric pyridine case but that the band energy has actually dropped substantially compared to that of the Creutz–Taube ion. From this we conclude that the redox asymmetry is important in determining both bandwidth and band position.

The redox potential shift ratio m (defined by $\delta[E_{1/2}(\mathrm{Ru_a})]/\delta[E_{1/2}(\mathrm{Ru_b})]$ relative to the first and second peaks for $\mathrm{[Ru(NH_3)_5]_2pyz^{4+/5+/6+}}$) is highest for the two dimers bearing the smallest $\delta[E_{1/2}(\mathrm{Ru_b})]$, $\Delta\nu_{1/2}$, and $\Delta E_{1/2}$ values. This would be expected if indeed m is responsive to the degree of metal–metal interaction. A related observation is the fact that the m' values for the second series (now defined by $\delta[E_{1/2}(\mathrm{Ru_b})]/\delta[E_{1/2}(\mathrm{Ru_a})]$ relative to $\mathrm{(bpy)_2ClRu(pyz)Ru(NH_3)_5}^{3+/4+/5+}$) are considerably diminished compared to the m values obtained in the first series. These ions are clearly class II as evidenced by the fact that they exhibit IT bands somewhat wider than predicted by Hush theory.[2,10] The strong nature of the coupling in the first series is forcefully demonstrated by the fact that a perturbation of as much as 0.171 V in the energy of the mixed-valence ground state (as reflected in $\delta[E_{1/2}(\mathrm{Ru_b})]$ for L = bpy) results in an increase of only 0.024 V in redox asymmetry as measured by $\delta[\Delta E_{1/2}]$. The delocalized to localized transition in electronic structure down the series is supported by the fact this modest increase in redox asymmetry brings about an increase in E_{IT} of 0.31 eV.

The ratio m can be related to the ratio of variational wave function coefficients ρ as defined in the Mulliken treatment of donor–acceptor interactions[7,8,11,12]

$$\Psi_g = a\Psi^\circ_1 + b\Psi^\circ_2 \tag{1}$$

$$\rho = b/a \tag{2}$$

where Ψ°_1 would represent the limiting, zero-order wave function with the odd electron totally localized on the $\mathrm{Ru_b}$ fragment and the pyrazine bridge. This situation can be modeled via the rhodium analogues *trans*-$\mathrm{Ru_b^{II}L(NH_3)_4pyzRh^{III}(NH_3)_5^{5+}}$ (see ref 4 and 14 for applications of this strategy; see also ref 3). Ψ°_2 would represent localization on $\mathrm{Ru_a}$ and pyrazine with the whole complex distorted so as to be in maximum vibrational overlap with Ψ°_1. If the energies of Ψ°_1 and Ψ°_2 are denoted by E°_1 and E°_2 and their difference by Δ, the variational energy roots are found to be

$$E_\pm = \frac{1}{1 - S^2}\left[\frac{E^\circ_1 + E^\circ_2}{2} - SH \pm \left(\frac{\Delta^2}{4} + \beta_1\beta_2\right)^{1/2}\right] \tag{3}$$

where S is the overlap integral $\langle\Psi^\circ_1|\Psi^\circ_2\rangle$, H is the resonance integral $\langle\Psi^\circ_1|\hat{H}|\Psi^\circ_2\rangle$, $\beta_1 = H - E^\circ_1S$, and $\beta_2 = H - E^\circ_2S$. The ratio ρ is given by Mulliken as

$$\rho = \frac{E_- - E^\circ_1}{H - SE_-} = \frac{SE_- - H}{E^\circ_2 - E_-} \tag{4}$$

Manipulations of (3) and (4) lead to the result[15]

$$\rho = \left[\frac{m\Delta + 2HS - S^2(2E_1 + \Delta(1 + m))}{\Delta + 2HS - 2S^2E^\circ_2}\right]^{1/2} \tag{5}$$

In the limit of small S, this reduces to the particularly simple result

$$\rho = m^{1/2} \tag{6}$$

In the case of the pyrazine-bridged complexes considered here, it is likely that the strong metal-to-bridging-ligand π back-bonding results in a substantial degree of electronic overlap between Ψ°_1

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and $\Psi°_2$.[16,17] As an example of this effect, we note that if S is allowed to be as large as 0.2 the calculated value of ρ for the *trans*-(3-F-py)$(NH_3)_4Ru^{II}pyzRu^{III}(NH_3)_5{}^{5+}$ dimer changes from 0.91 to 0.96.[18] The result that the values of ρ obtained at the narrow $\Delta\nu_{1/2}$ end of the first series are essentially equal to 1 supports a class III electronic structure for the Creutz–Taube ion. ρ values of the more perturbed end of the series are closer to 0.9 and indicate a transition toward a localized description. This is in agreement with the trend evidenced by the spectral data. In the class II molecules comprising the second series, it is found that ρ drops substantially to values more on the order of 0.4–0.5. This is also in accord with expectations based on the spectral observations.

It is interesting that m and ρ are as large as they are over the entire first series even though the $\Delta\nu_{1/2}$ values point toward a substantial class III to class II transition in electronic structure. Relevant to this point, investigation of the solvent dependence of E_{IT} for some of the members of this series as well as further investigation of symmetrically substituted species is under way. Other work in progress includes precise determination of intervalence-transfer band extinction coefficients for the dimers reported here, extension of this approach to other bridging ligands such as 4-cyanopyridine and 4,4'-bipyridine, a comparison of the effects of cis vs. trans substitution at the directly perturbed metal center, and electrochemical investigation of various rhodium–ruthenium analogues.

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Supplementary Material Available: Detailed derivation of eq 5, a figure showing potential curves for an asymmetric, predominantly localized system, and a listing of microanalytical data (7 pages). Ordering information is given on any current masthead page.

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A Novel μ-Terephthalato Copper(II) Dimer with Unexpected Strong Antiferromagnetic Exchange Interaction

Sir:

In our laboratory a research project aimed at investigating the factors affecting the superexchange interactions propagated by multiatom bridges is under way.[1,2] Within this framework a series of new μ-terephthalato copper(II) binuclear complexes has been chosen and thoroughly investigated by using both experimental and theoretical approaches. Most of these new d^9–d^9 magnetic systems exhibited negligible intramolecular exchange interactions but showed weak intermolecular antiferromagnetic interactions ($2J$ values in the range -1.00 to -5.06 cm^{-1}), depending on the transition-metal ground state. Similar results were reported recently by Kahn et al.[3] for three analogous compounds. The magnetic behavior of all these compounds was also predicted by EHMO calculations performed on a series of model compounds exhibiting a variety of transition-metal ground states.[2,4] Contrary to our quantum-chemical predictions, the dimer (μ-terephthalato)bis[(2,2'-bipyridine)aquocopper(II)] dication, in its salt form with perchlorate anions, $[Cu_2(\mu\text{-TPHA})(bpy)_2(OH_2)_2](ClO_4)_2$ (**1**) (where TPHA = terephthalato and bpy = 2,2'-bipyridine), exhibited an unexpected stronger antiferromagnetic interaction ($2J$ value of -51.8 cm^{-1}).

In this communication the experimental and theoretical data available accounting for this stronger antiferromagnetic interaction of complex **1** are presented. It proves to be intermolecular in nature.

Complex **1** was prepared by adding a solution of 0.336 g (1 mmol) of piperidinium terephthalate and 0.312 g (2 mmol) of 2,2'-bipyridine in methanol (10 mL) to a solution of 0.74 g (2 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$ in the same solvent (6 mL), at room temperature. The blue microcrystalline product formed gave satisfactory elemental analysis corresponding to the formula $[Cu_2(\mu\text{-TPHA})(bpy)_2(H_2O)_2](ClO_4)_2$. Numerous attempts in our laboratory to grow single crystals suitable for a structural investigation have been unsuccessful so far.

The IR spectrum of **1** exhibited the $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ strong absorption bands due to the terephthalato ligand, along with the characteristic bands of the noncoordinated perchlorate anions.[5] The absence of any splitting of the $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ bands strongly suggests the end-to-end linking of the terephthalato ligand in an equivalent way at both sites. Furthermore, the observed $\nu_{as}(CO_2)-\nu_s(CO_2)$ value of 182 cm^{-1} calls for an ambidentate bonding mode[6] of the carboxylato groups.

The electronic reflectance spectrum of the complex exhibited in the visible region a broad band envelope with a maximum at 15.62×10^3 cm^{-1} and two shoulders at 17.00×10^3 and 13.23×10^3 cm^{-1}, respectively. According to the well-established electronic criteria of stereochemistry for Cu(II) compounds,[7] this spectrum is at first sight characteristic of five-coordinated Cu(II) chromophores with distorted square-pyramidal configuration. However, the appearance of the shoulder at 17.00×10^3 cm^{-1} provides evidence for the presence of six-coordinated chromophores with strongly distorted elongated octahedral configurations. The coexistence of both five- and six-coordinated chromophores in **1**, although prohibited by the stoichiometry and the bonding mode of the ligands in the binuclear complex, could be explained on the grounds of intermolecular solid-state interactions. Therefore, the formation of dimers or polymers in the solid state involving both types of coordination could not be excluded. These intermolecular solid-state interactions are accounted for by the nature and energies of the frontier MO's of **1** calculated on the basis of the EHMO method. It is obvious that the frontier MO's that would be responsible for the solid-state interactions of the isolated binuclear entities are only those exhibiting significant metal $3d_{z^2}$ and ligand p_z character. For **1** these MO's were the HOMO and LUMO with significant metal and ligand character, respectively. These HOMO–LUMO orbital interactions lead to the formation of a dimeric (**2**) or polymeric (**3**) structure (see Chart I) and account for the coexistence of both the five- and six-coordinated chromophores in the solid state. Moreover, the dimerization or polymerization of the binuclear moieties is also favored by their planarity due to the extensive conjugation encountered for both

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